

Femtosecond Photoionization Studies of the Photodissociation of Acetone

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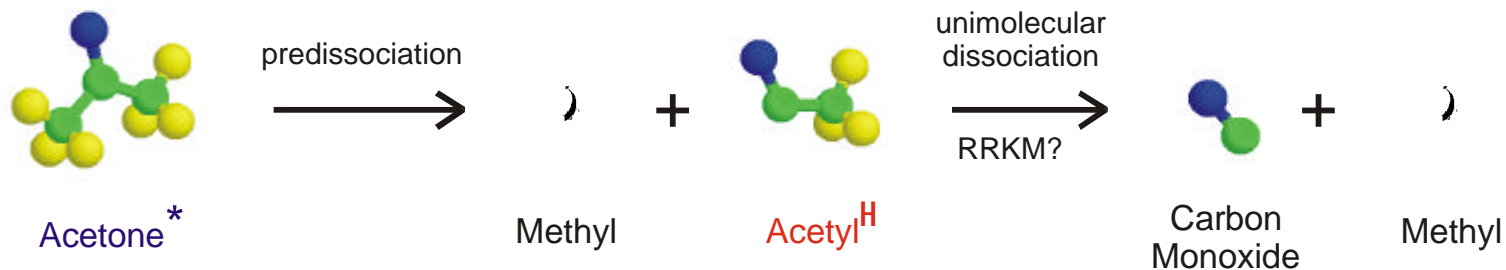


ABSTRACT

The photodissociation dynamics for the S_1 valence state and the S_2 , $3s$ Rydberg state of acetone (h_6 and d_6) have been studied using femtosecond mass-resolved photoionization spectroscopy. The S_2 excited state lifetime measured for acetone- d_6 using 194 nm pump/257 nm probe is 13.5 ± 1.0 ps, which is almost three times longer than we previously determined for this state in acetone- h_6 , 4.7 ± 0.2 ps.¹ The secondary dissociation time for acetyl- d_3 measured with 388 nm two-photon ionization probe is 3.0 ± 0.5 ps, similar to our result for acetyl- h_3 (3.1 ± 0.5 ps).¹ RRKM calculations predict acetyl- h_3 to be faster, suggesting differences in the primary energy partitioning and/or a secondary dissociation reverse isotope effect. The S_1 state dynamics were investigated by near UV pump (270 nm)/deep UV probe. The primary dissociation time is instrument-limited, providing a 200 fs upper limit to the lifetime. The acetyl ion signal exhibits a subpicosecond decay and a persistent signal. The former is consistent with results from Kim and Zewail² for two photon excitation to near the $4s$ state. The persistent signal is attributed to probe induced ionization of stable acetyl radicals, consistent with previous results³ (that indicate low internal energy). In addition, similar studies on acetic acid and acetyl cyanide indicate that the primary dissociation is prompt in both cases and the acetyl secondary dissociation times are 5 ps and 0.5 ps, respectively. Product energy distributions are well determined,^{4,5} so it is possible to demonstrate the importance of using a distribution averaged $k(E)$ rather than using single energy point rate $k(\langle E \rangle)$ to obtain good agreement with the measured value.

Introduction - Photochemistry of Acetone

- ▶ Benchmark for multiple dissociation - two equivalent bonds; simplest ketone
- ▶ All states investigated so far undergo **STEPWISE** dissociation
- ▶ Testing ground for accurate description and suitable models for photodissociation
 - Energy partitioning and nonstatistical secondary dissociation
 - fragment internal energies dictate dissociation times
 - statistical behavior possible for longer dissociation times (IVR>diss.)
 - Complimentary experimental approaches:
 - product energy distributions P(E) & time-resolved studies of lifetimes (τ)
 - clear and quantitative nonstatistical behavior requires knowledge of P(E)
- ▶ Until recently, **NO** product and ultrafast studies on same excited state



Acetone Spectroscopy

Spectroscopy of S₁ State

- ▶ ¹(nπ*) or \tilde{A} state: strong coupling with nearby triplet → mixed {S₁T₁} state
- ▶ Broad and unstructured band centered at 280 nm; origin at 328 nm
- ▶ Dissociation threshold at 306 nm; barrier to dissociation (13.4 kcal/mole)⁵
- ▶ Excited state lifetimes from fluorescence quantum yield:
<1.6 ns @ 260 nm⁶ ⇒ Often quoted as 1 ns !!!
- ▶ Isotropic transition moment near dissociation threshold^{7a}

Spectroscopy of S₂ State

- ▶ 3s Rydberg or \tilde{B} state: promotion of oxygen electron: n⇒3s
- ▶ Absorption bands (180-195 nm; origin at 195 nm for h₆, 194.5 for d₆)
 - vibronic structure but rotationally/torsionally diffuse ⇒ predissociation
 - 17 cm⁻¹ linewidths from jet-cooled spectra⁸ ⇒ lifetime ≥ 300 fs
 - acetyl intermediate indicated by MPI power dependence^{7b}

Product Translational and Internal Energy-Resolved Studies

S₁ State

- ▶ Partial acetyl secondary dissociation ($30 \pm 4\%$ at 248)³ - *stepwise* dissociation
- ▶ CH₃ translation energy peaks resolved^{3,9}
- ▶ Primary translation energy insensitive to excitation energy: exit barrier effects³
- ▶ Isotropic angular product distribution^{3,9}

S₂ State

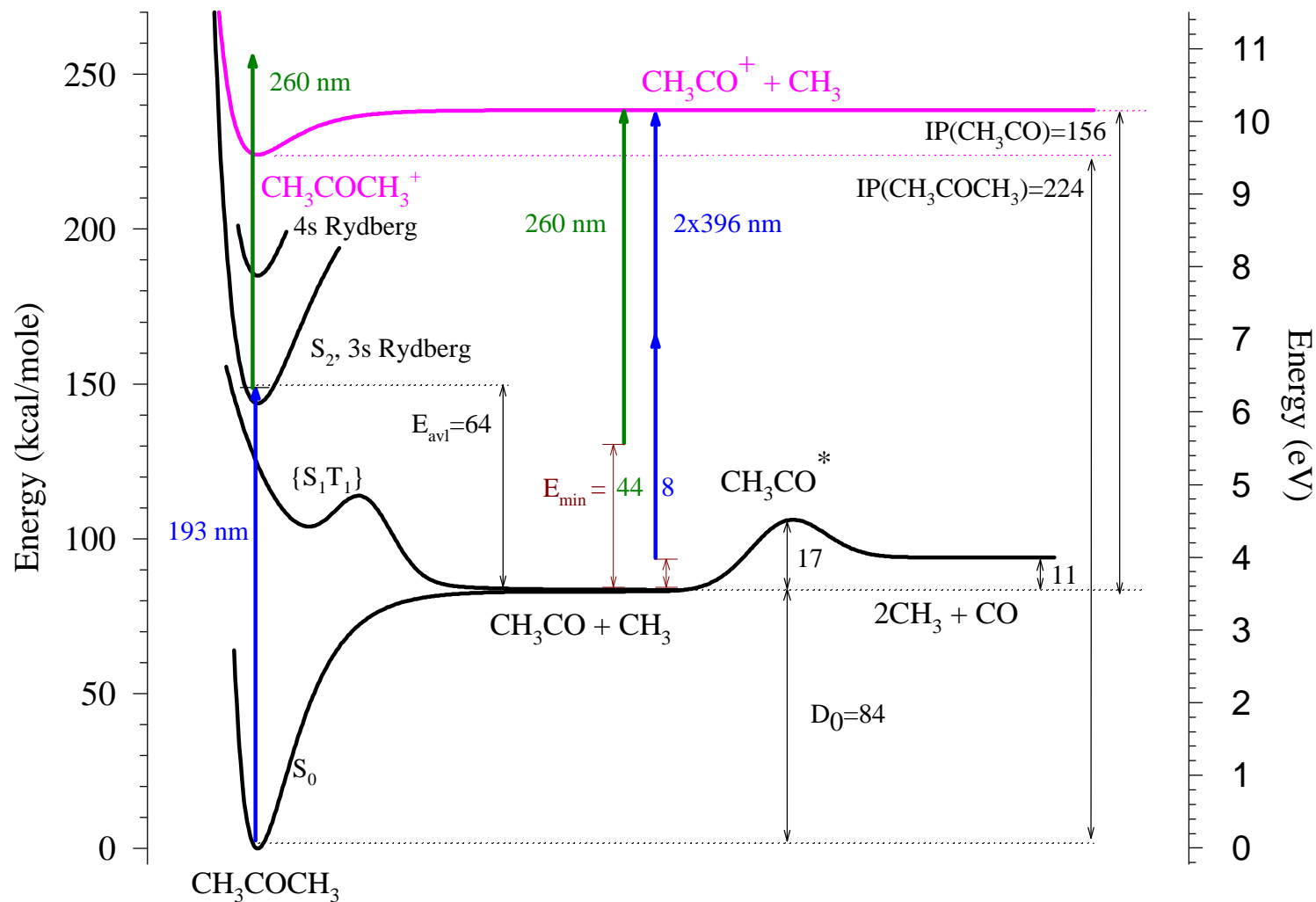
- ▶ Near unity quantum yield¹⁰ for dissociation to 2CH₃ + CO:
- ▶ Stepwise mechanism suggested:
 - high rotational temperatures in products¹¹
 - two CH₃ translational energy distributions from analysis
- ▶ Higher methyl internal energy measured recently^{12a} than previously^{12b}
 - neither impulsive nor statistical models account for energy distributions
 - **considerable uncertainty remains about primary methyl E_{int} (-> E_{int})**
- ▶ Isotropic angular product distribution³

17±1 kcal/mole barrier to acetyl dissociation: photofragment translational spectra¹³

Mass-Resolved Ultrafast Studies

- ▶ Kim *et al.*²: 2 photon excitation with 307 and 280 nm to **near 4s state** (also d₆)
 - stepwise; acetone fast (<50 fs); acetyl: 500 fs at 2×307nm, 180 fs for 2×280 nm
 - rates: RRKM-like with impulsive partitioning; track RRKM vs. exc.& isotope
 - acetyl from MEK, DEK, acetyl chloride^{2b}; assess E_{int} from k_{RRKM}
- ▶ Buzza *et al.*¹⁴: 3+2 MPI with 585 nm to S₂ (?)
 - acetone - not observed at parent ion, instrument-limited (<100 fs) from acetyl
 - 1.7 ps dissociation time for acetyl monomer close to their RRKM calculation
 - minimum internal energy too high for proposed excitation/ionization scheme
- ▶ Shibata and Suzuki¹⁵: S₁ by near UV excitation, mass-resolved imaging
 - instrument limited acetone parent & partially persistent acetyl
 - interpreted as long acetone lifetime (<15 ps): acetyl ion from diss. ionization
- ▶ Owrutsky and Baronavski¹: 193+260/386 nm to S₂
 - S₂ dissociation is stepwise
 - 4.7 ps lifetime for S₂ and 3.1 ps secondary acetyl dissociation time

Potential Energy Surfaces for Acetone Photodissociation



Reaction Scheme in Acetone Photochemistry

CH_3COCH_3	193-195 nm \Rightarrow	$\text{CH}_3\text{COCH}_3^*$	Absorption
$\text{CH}_3\text{COCH}_3^*$	260 nm \Rightarrow	$\text{CH}_3\text{COCH}_3^+$	Parent Ionization
$\text{CH}_3\text{COCH}_3^*$	k_p \Rightarrow	$\text{CH}_3\text{CO}^\dagger + \text{CH}_3$	Predissociation
$\text{CH}_3\text{COCH}_3^+$	k_{di} \Rightarrow	$\text{CH}_3\text{CO}^+ + \text{CH}_3$	Dissociative Ionization
$\text{CH}_3\text{CO}^\dagger$	k_d \Rightarrow	$\text{CH}_3 + \text{CO}$	Acetyl Dissociation
$\text{CH}_3\text{CO}^\dagger$	260 nm \Rightarrow	CH_3CO^+	Neutral Acetyl Ionization

* Electronically excited

† Vibrationally excited

Mass-Resolved Femtosecond Photoionization Spectroscopy

Experimental Approach

- ▶ Pump & probe fs laser pulses:

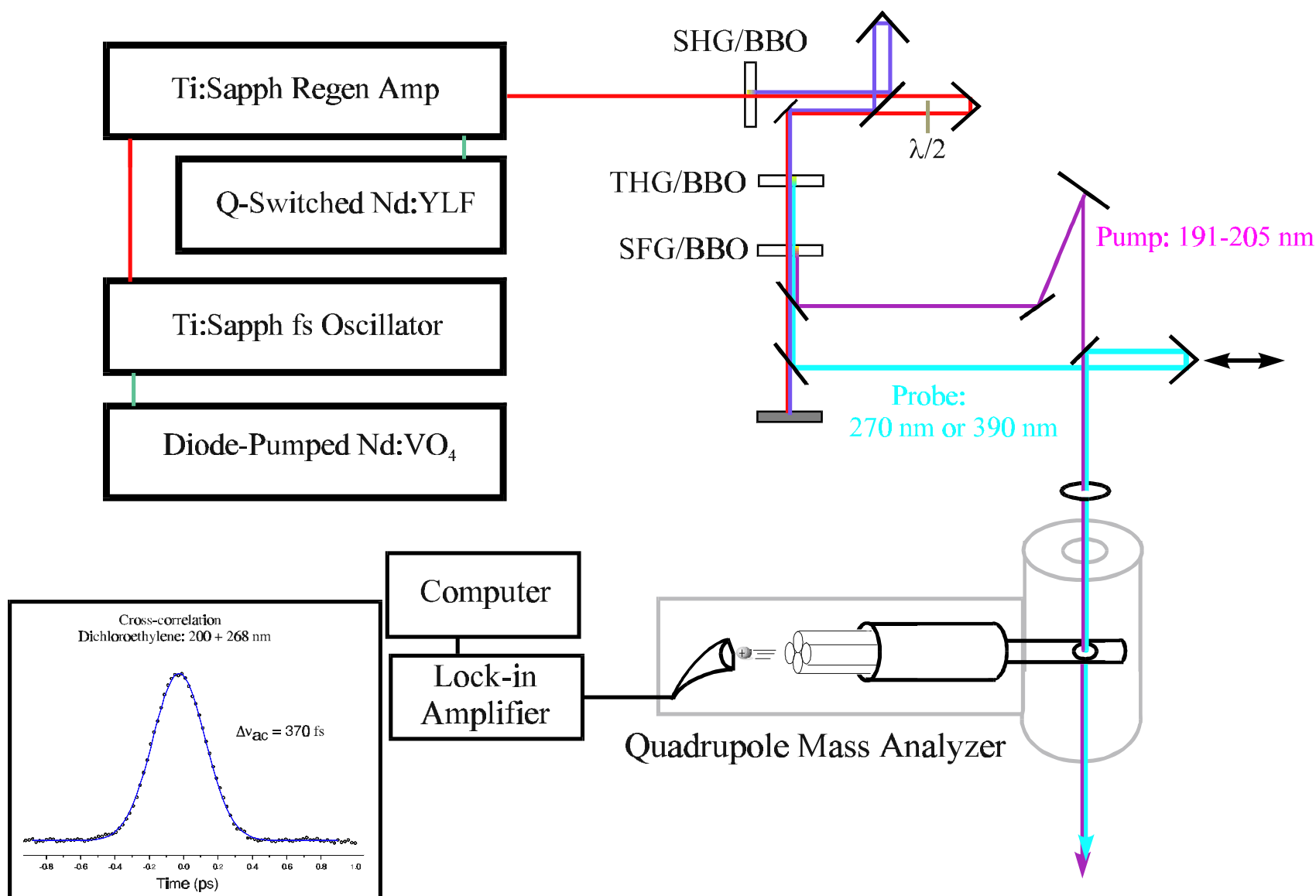
Harmonics of regeneratively amplified Ti:Sapphire (800 nm (fund.) - - 200 nm (4th))

- ▶ Mass resolved detection with quadrupole mass spectrometer; effusive source

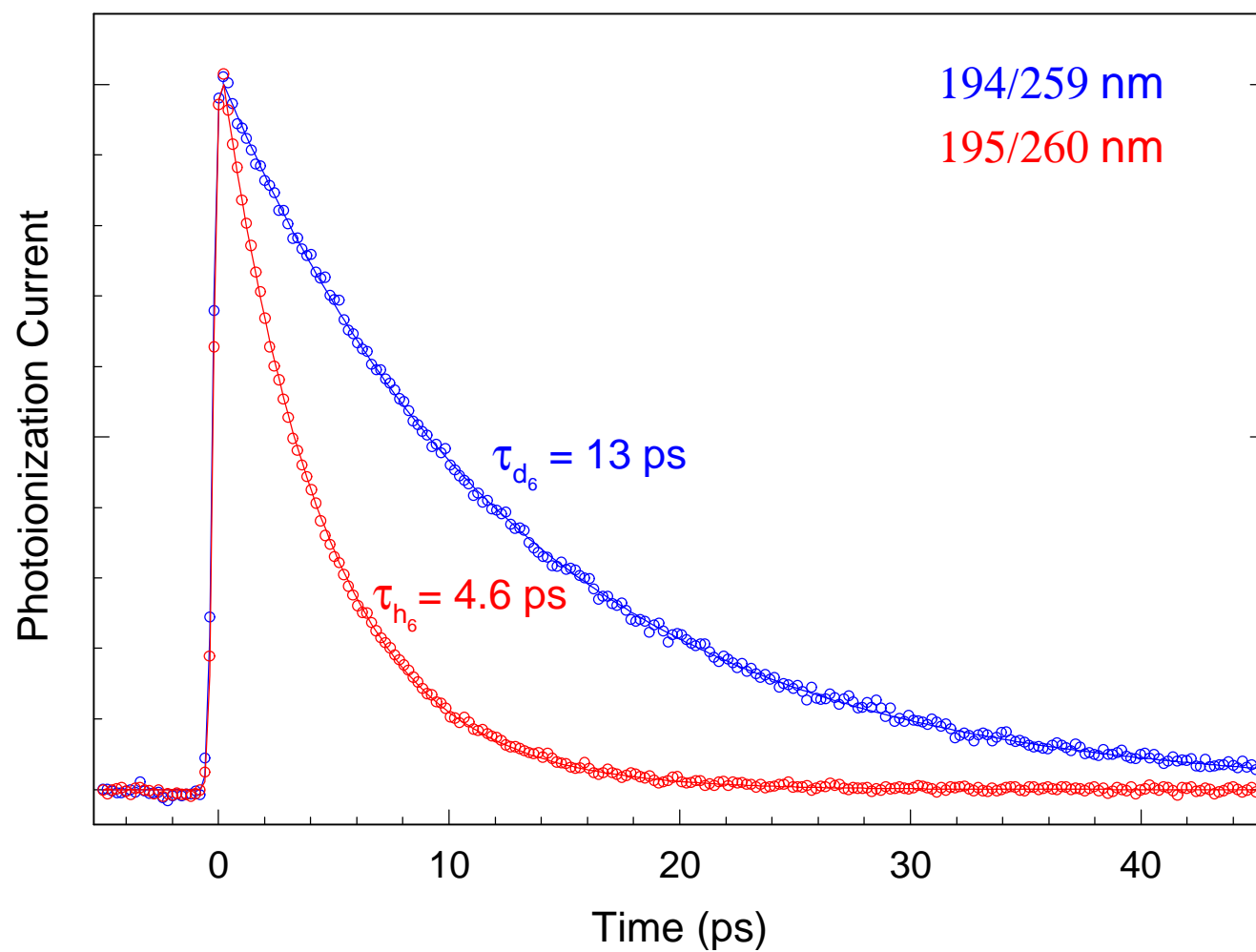
Excitation and Probe Laser Wavelengths

	Excitation	Probe
S₁ Valence	Near UV (~270 nm) [2 photon Near UV]	Deep UV (200-205 nm); Blue (400-410 nm)
S₂, 3s Rydberg	Single photon deep UV (193-195 nm)	Near UV (260 nm) for acetone Blue (390 nm) for acetyl

Apparatus for Deep UV Femtosecond Mass Resolved Photoionization Spectroscopy

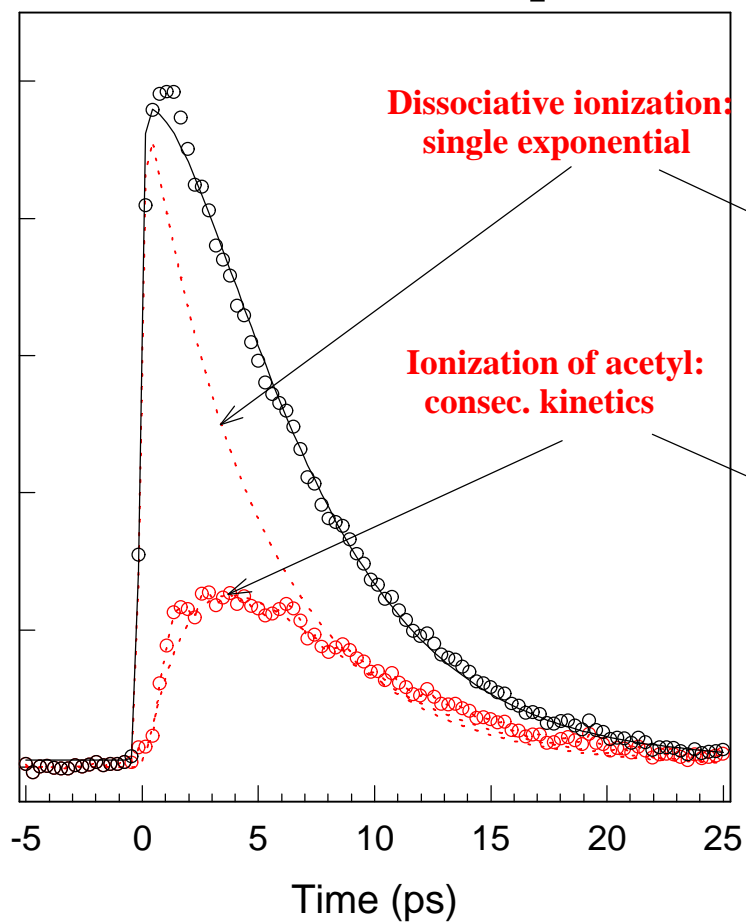


Primary S₂ Dissociation for Acetone (**h**₆ and **d**₆)

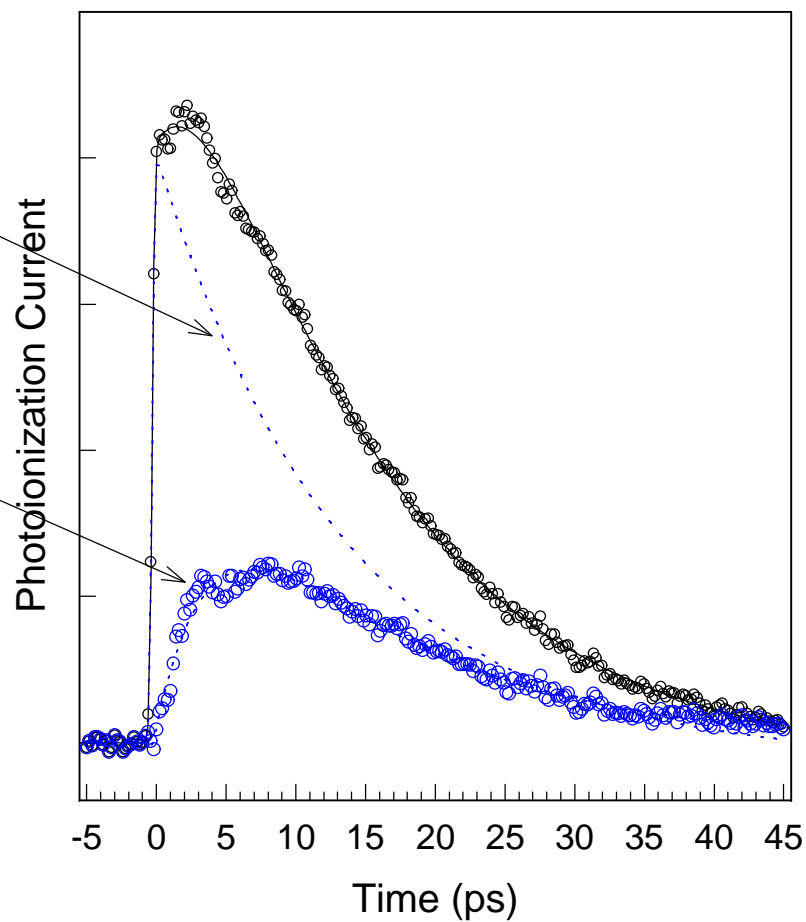


Secondary Dissociation of Acetyl after S_2 Excitation of Acetone

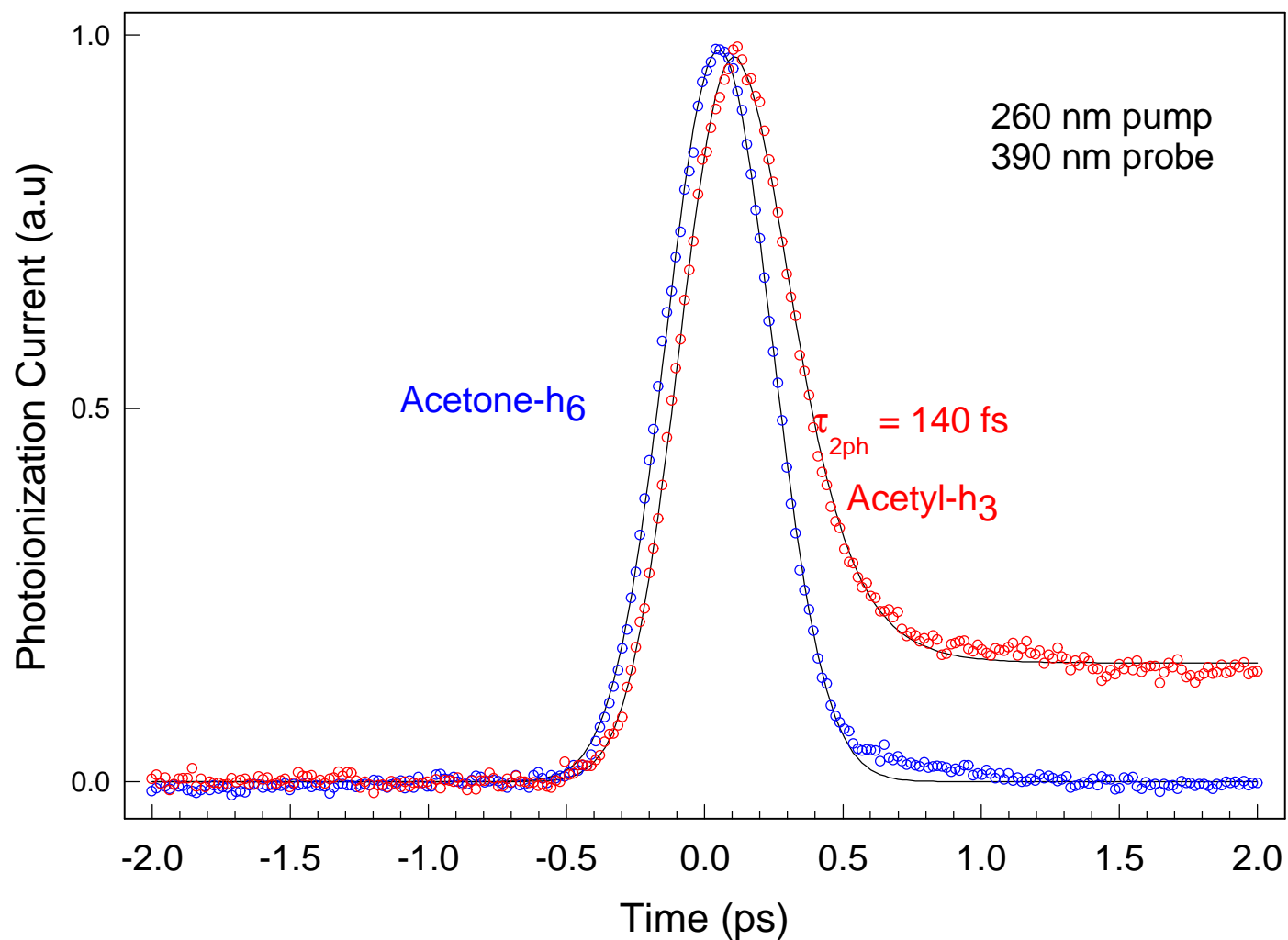
Acetyl- h_3
 $t = 3.1 (0.5) \text{ ps}$



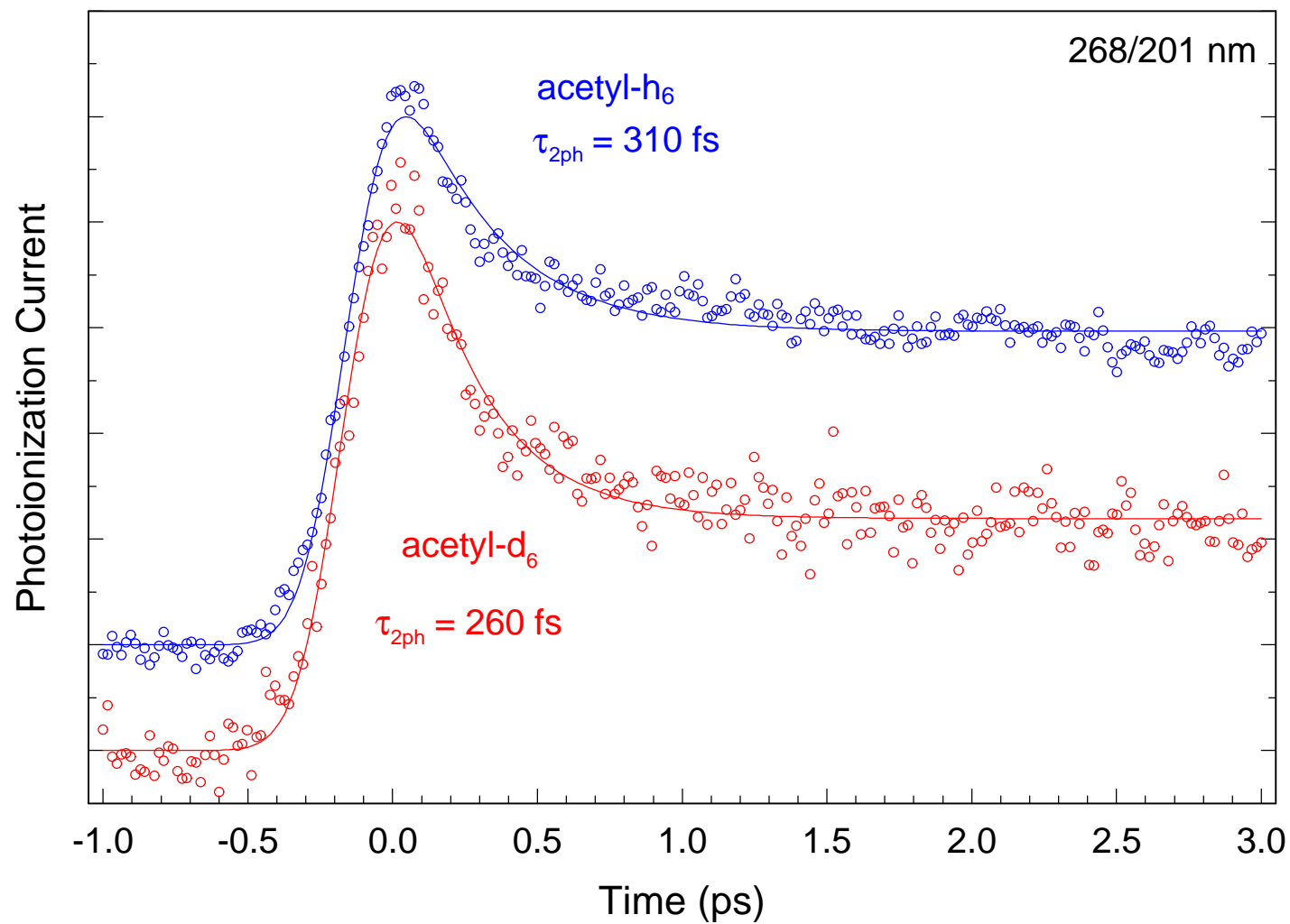
Acetyl- d_3
 $t = 3.0 (1.0) \text{ ps}$



Acetone-h₆ Dissociation with Near UV Pump



Secondary Acetyl Dissociation for Near UV Pump



Results Summary and Analysis

Data Analysis for S₂:

Parent: single exponential

Acetyl with 386 nm probe:

single exponential +
consecutive decay kinetics

$$S(t) \propto f_{cons} \left(\frac{e^{-k_p t} - e^{-k_d t}}{k_d - k_p} \right) + (1 - f_{cons}) e^{-k_p t}$$

	Photoion Detected	Pump (nm)	Probe (nm) [E _{min} (acetyl),eV]	Signal Description	Decay Time (ps)	
					H	D
S ₂	Acetone	193-195	260/2x386	single exp.	4.7 ± 0.2	13.5±1.0
	Acetyl	193-195	260 [1.9]	single exp./DI	↑	↑
	Acetyl	193-195	2x386 [0.34]	s. exp. + cons.	3.1±0.5	3.0±0.5
S ₁	Acetone	267-273	202-205/2x404	inst.-limited	<0.2	<0.2
	Acetyl	267-273	202-205/2x404 [0.4]	subps + persis	>150	>150

Energy Partitioning and RRKM Rates

RRKM dissociation rates: calc'd with *UNIMOL program suite*¹⁶ (vib. frequencies-Deshmukh et al.¹⁷)

Energy partitioning: $E_{av1} = E_{hv} - D_o[83.7 \text{ kcal/mole}]$

E_{av1} @268nm (S_1) = 24 kcal/mole; E_{av1} @193nm (S_1) = 64 kcal/mole

From Product Energy Distributions:

$$\langle E_{int}(CH_3CO) \rangle_{193nm} = E_{av1} - \langle E_T \rangle [14.2]^3 - \langle E_{int}(CH_3) \rangle [12 \pm 5(??)] = 37.7 \pm 5$$

Impulsive model:

E_{av1} partitions between dissociating atoms and then to fragments:

$$E_{int}(CH_3CO) = (1 - M_C/M_{CH_3CO})(M_C/\mu_{C-C})E_{av1}$$

$$E_{int}(CH_3CO) / E_{av1} = 0.36 \text{ (0.37 for } d_3)$$

Statistical model:

Energy partitioned equally into all vibration modes (s) - *Simple* treatment:

$$E_{int}(CH_3CO) = [s(CH_3CO)/s(CH_3COCH_3)]E_{av1}$$

$$E_{int}(CH_3CO) = 0.5 E_{av1}$$

Excited State	Impulsive				Statistical			
	E_{int} (kcal/mole)		$\tau(E_{int})$ (ps)		E_{int} (kcal/mole)		$\tau(E_{int})$ (ps)	
	h_3	d_3	h_3	d_3	h_3	d_3	h_3	d_3
S_1@248	8.6	8.9	-	-	12	12	-	-
S_2@194	23.4	23.0	6.9	20.7	32	32	0.6	1.1

Discussion: S_1 State Photodissociation

- ▶ Similar signals for 260-268 nm excitation with 200 or 400 nm probe
- ▶ Two photon to/near 4s Rydberg - agrees with Kim et al.² (fast acetone, subps acetyl)
- ▶ Single photon to S_1
 - **acetone dissociation - instrument-limited**, prompt: <200 fs lifetime upper limit
 - no persistent long-lived component
 - **acetyl ion** signal (>150 ps) **long lifetime** or stable
 - from product studies: stepwise mechanism,
low acetyl E_{int} (~ 10 kcal/mole) and <1% acetyl dissociation
- ▶ Relationship to previous results:
 - Consistent with Breuer and Lee's nanosecond **UPPER LIMIT** and broad band
 - Isotropic products - from isotropic transition moment rather than long lifetime
 - Decays for acetone and acetyl similar to Shabata and Suzuki,¹⁵
 - they attribute to dissociative ionization (because isotropic and slow)
 - simplest explanation is short lifetime; diss. ion. not complete for other states (S_2)

Discussion: Primary S₂ Photodissociation Dynamics

- ▶ Sequential dissociation mechanism, primary and secondary steps temporally resolved
- ▶ Acetone S₂ state lifetime:
 - Long Lifetime:
 - time for vibrational energy redistribution - consider fully statistical mechanism
 - explains isotropic products
 - consistent with limits from absorption linewidths
 - **LARGE (~×3) ISOTOPE EFFECT**
 - similar to isotopic lifetimes effects for S₁ at dissociation limit^{5b}
 - also observed for other molecules: NH₃, CH₃I (higher Rydbergs)
 - tunneling over torsional barrier?

Discussion: Secondary Dissociation Dynamics

- Acetyl dissociation -

- S faster than primary acetone dissociation, especially for deuterated species

- S Same rates for h_3 and d_3 : no *apparent* isotope effect in secondary dissociation

- S $E_{\text{int}}(\text{acetyl})$ at 193 nm uncertain

- For $\langle E_t \rangle = 14.2 \text{ kcal/mole}$, IF $E_{\text{int}}(\text{CH}_3) = 12 \pm 5 \text{ kcal/mole}$,

- $E_{\text{int}}(\text{acetyl}) = 38 \pm 5 \text{ kcal/mole}$; $k(E) < 1 \text{ ps}$

- no quantitative determination of non-RRKM behavior

- S RRKM rates: d_3 **slower** at same E_{int} - **reverse isotope effect observed**

- $E_{\text{int,inf}}$ - inferred from rate:

- h_3 - 3.1 ps \Rightarrow 25 kcal/mole; d_3 - 3.0 ps \Rightarrow 26.8 kcal/mole** (d_3 @ 25 kcal/mole = 8.4 ps)

- S Either 1) isotope dependent energy partitioning:

- more time for d_3 - more statistical, E_{int} ?

- And/or 2) isotope dependent dynamics - isotope dependent nonstatistical effects

- faster IVR for lower frequency acetyl- d_3 modes?

- No dissociation model accounts for all data:

- $E_{\text{int}}(\text{CH}_3)/E_{\text{int,inf}}(\text{acetyl})$ too high - non-RRKM

Acetyl Unimolecular Decomposition: RRKM Rates

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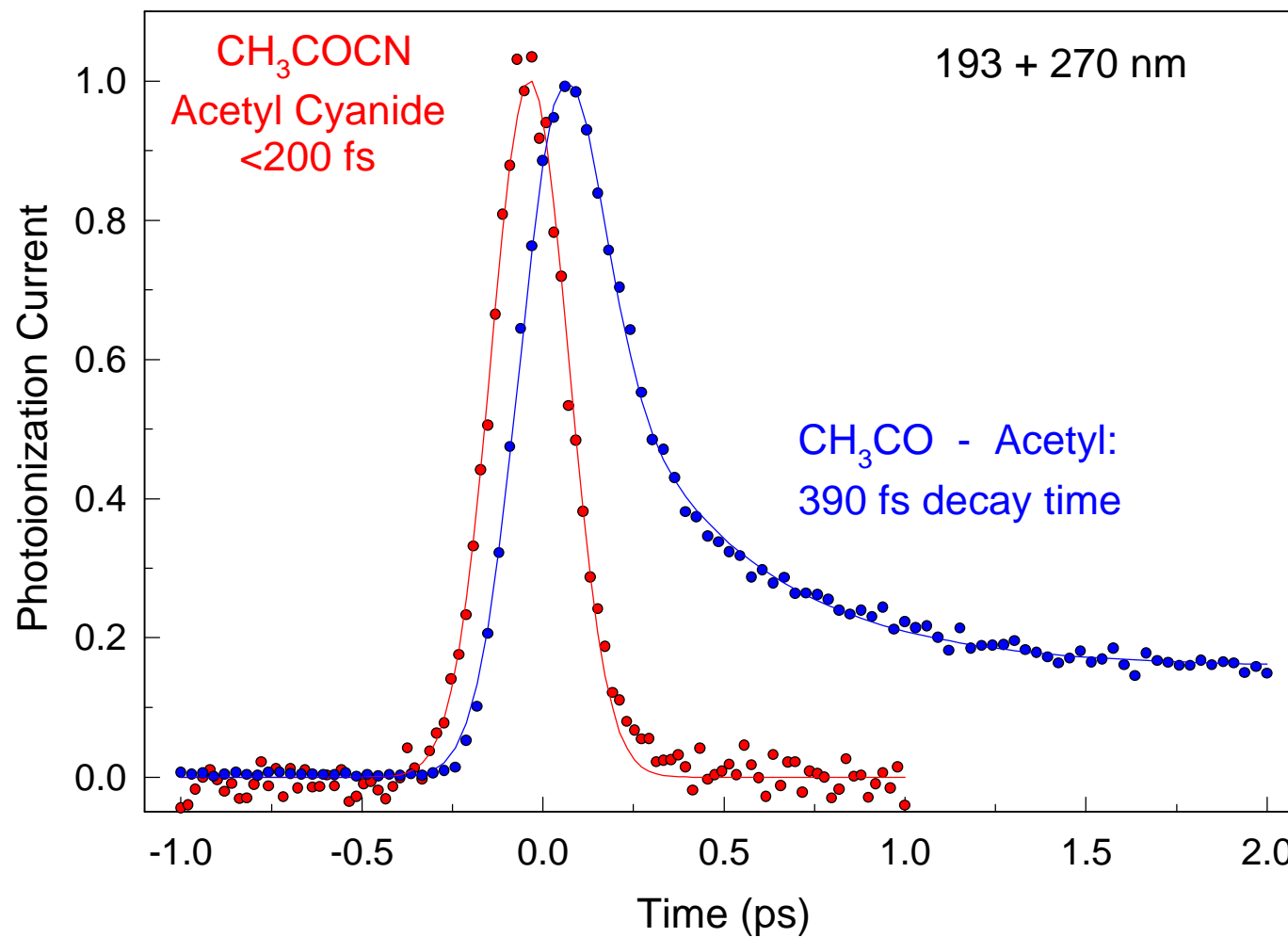
Background:

The observed lifetime of acetyl (3.1 ps) from the photodissociation of acetone at 193nm is much longer than predicted by RRKM calculations (1 ps) using the best estimates available for the internal energy in acetyl.

Recently, there has been interest in molecules which exhibit “non-RRKM” behavior; i.e., those for which IVR may be slow with respect to dissociation(Thompson; Wolynes).

We hoped that by using precursors whose acetyl partner fragment internal energy was much better characterized, we would be able to more accurately assess the RRKM behavior of the acetyl decomposition.

Photodissociation of Acetyl Cyanide and Secondary Acetyl Decomposition



RRKM Lifetimes and $\langle E_{\text{int}} \rangle$

$\langle E_{\text{int}} \rangle$ (kcal)	Precursor	$\tau_{\text{int}}(\text{psec})$	$\tau_{\text{dist}}(\text{psec})$	$\tau_{\text{obs}}(\text{psec})$
19.6	CH ₃ COOH	100.	6.2	5. (1)
31.0	CH ₃ COCN	0.74	0.56	0.56
31.4	“	0.70	0.53	0.52
31.7	“	0.63	0.50	0.46
32.1	“	0.60	0.47	0.39
35.0	CH ₃ COCl	0.38	0.38	?

- ! Agreement between predicted lifetimes at the average internal energy and observed lifetimes is poor, especially for acetic acid
- ! The agreement is greatly improved when the energy distribution in the acetyl is properly taken into account (the shape of the distribution).
- ! Therefore: $\text{Rate}^{\text{RRKM}}(\langle E_{\text{int}} \rangle) \quad \langle \text{Rate}^{\text{RRKM}}(E_{\text{int}}) \rangle$

Conclusions:

- ! Acetyl precursors with simple (diatomic) companion fragments and well characterized product energy distributions permit quantitative investigation of dissociation dynamics**
- ! By including (in some fashion) the energy distribution in acetyl, rather than just the average internal energy, we obtain reasonable agreement with RRKM rates for acetyl from acetyl cyanide and acetic acid.**
- ! As expected, this kind of treatment will not help explain the data from acetone, where the acetyl RRKM lifetime is already shorter than what is observed.**
- ! There still remains the problem of HOW the acetyl is prepared: in acetone it is formed by predissociation from a Rydberg state; the others have not been determined, but may be $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$**

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